Benzyne by Pyrolysis of Phthalic Anhydride

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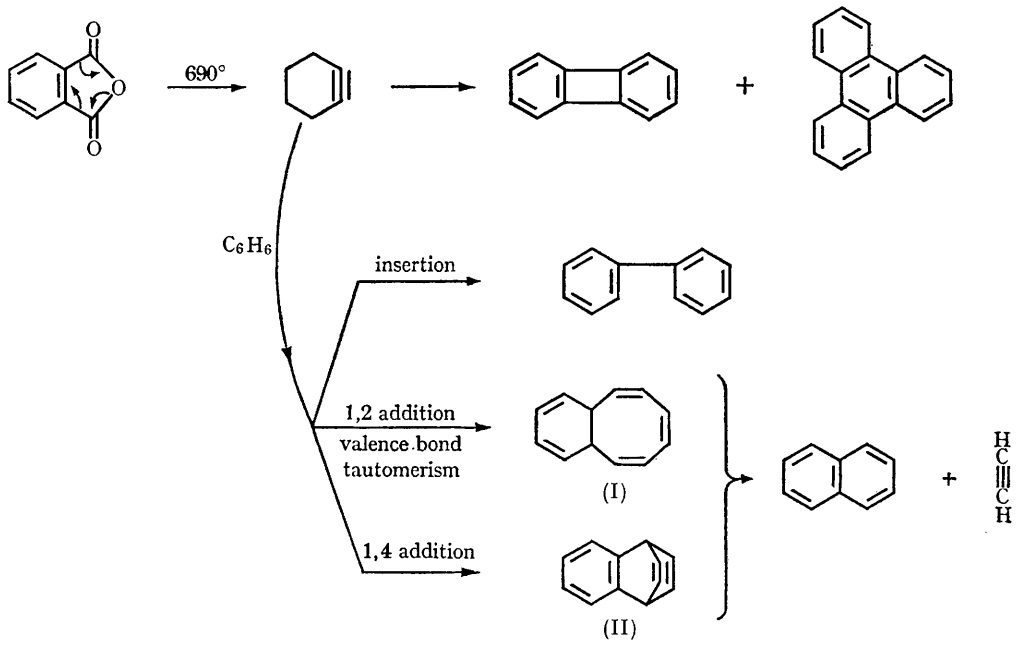
PHTHALIC anhydride upon electron impact loses consecutively carbon dioxide and carbon monoxide to give an ion of mass 76,[1,2] which we formulate most simply—although not unequivocally—as benzyne. In the hope of duplicating this reaction thermally, we pyrolyzed 100 ml. of a 0·1 molar solution of phthalic anhydride in benzene at 690° under nitrogen at a steady rate of 30 ml./hr. The pyrolysis tube was Vycor, filled with Vycor beads: contact time was 11·5 seconds, which gave a 58% conversion of the phthalic anhydride. Acetylene was steadily evolved and was identified in the gas stream by mass-spectral analysis of samples taken at regular intervals. The benzene was distilled off and the products boiling over 180°, 2 g., were analyzed by mass spectrometry on a Consolidated Model 21–103c instrument with the inlet system at 250°. The usual 70-volt spectrum was supplemented by a low-voltage (ionizing voltage 7·5, uncorrected) spectrum to help identify parent peaks. Final confirmation of the lighter and more abundant components was obtained by mass spectra of effluent from a gas-chromatographic column, measured "on the fly." In particular, this technique permitted unequivocal identification of biphenylene; both the spectrum and the retention time agreed precisely with those obtained by the same procedure on an authentic sample.

The major portion of the pyrolysate, apart from 0·62 g. of unconverted phthalic anhydride, was 1·05 g. of a mixture of naphthalene (15%) and biphenyl (85%). Benzene (100 ml.) pyrolyzed under identical conditions, gave no acetylene, and only 0·18 g. of high-boiling product, which consisted of about 96% (0·17 g.) biphenyl and 4% (0·072 g.) terphenyl. Only a trace of naphthalene (about 0·2%, 0·0004 g.), was found.

In addition to naphthalene and biphenyl, about 1% of biphenylene and 1% of product of molecular weight 228, possibly triphenylene, were found in the hydrocarbon portion of the phthalic anhydride pyrolysate. Neither was found in the benzene pyrolysis. These results indicate strongly that phthalic anhydride gives benzyne on pyrolysis, and

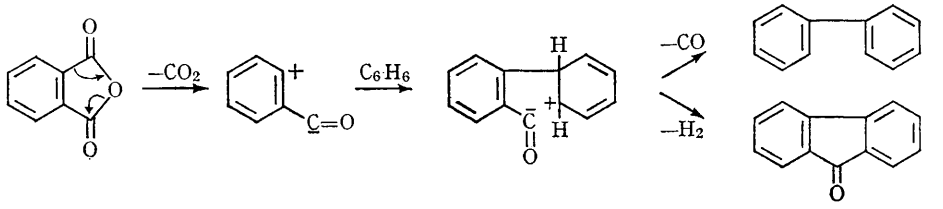
[1] F. W. McLafferty and R. J. Gohlke, *Analyt. Chem.*, 1959, **31**, 2076.
[2] S. Meyerson, *Rec. Chem. Progr.*, in the press.

suggest these reactions in the presence of benzene:



Biphenyl, benzocyclo-octatetraene (I), and benzobicyclo[2,2,2]octatriene (II) result from the reaction of benzyne (by decomposition of benzenediazonium carboxylate) with benzene at 45°.[3] Both (I) and (II) have given naphthalene and acetylene; (I) on photolysis,[4] and (II) in a sealed tube at 300°.[3]

The high ratio of biphenyl to naphthalene suggests perhaps stepwise, rather than concerted, loss of carbon dioxide and carbon monoxide from phthalic anhydride, similar to the mode of decomposition under electron impact.[2] The intermediate species could add to benzene to give biphenyl by subsequent loss of carbon monoxide or, alternatively by ring closure and loss of hydrogen:



Evidence for fluorenone as a minor product of the pyrolysis (a small peak at mass 180 that persists at reduced ionizing voltage) was indeed found. Direct-coupled gas chromatography–mass spectrometry clearly identified a minor component as fluorenone; and a precise mass-measurement on a high-resolution mass spectrometer[5] established $C_{13}H_8O^+$ as the empirical formula of the major component of nominal mass 180.

The nature of these reactions is being examined

[3] R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, 1963, **85**, 1798.
[4] G. J. Fonken, *Chem. and Ind.*, 1963, 1625.
[5] High-resolution data were obtained on the A.E.I. MS9 instrument in the Chemistry Department of the University of Chicago. We are indebted to the Department for making the instrument available to us, and to S. Greenberg for assistance in making the measurements.

by pyrolysis of phthalic anhydride with deuterated benzene, as well as with other aromatic systems. With pyridine, for example, phthalic anhydride at 690° gives, *inter alia*, phenylpyridine and a mixture of quinoline and isoquinoline, the analogues of biphenyl and naphthalene in the benzene reaction.

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